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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
 R factor = 0.046
 wR factor = 0.078
Data-to-parameter ratio = 15.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.*trans*-Bis[4-amino-3,5-bis(2-pyridyl)-4*H*-1,2,4-
triazole- $\kappa^2\text{N}^1, \text{N}^5$]bis(nitrato- κO)copper(II)

The crystal structure of the title compound, $[\text{Cu}(\text{NO}_3)_2(\text{C}_{12}\text{H}_{10}\text{N}_6)_2]$, consists of neutral mononuclear molecules held together by means of an extensive three-dimensional network of $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, $\text{C}-\text{H}\cdots\text{O}$ interactions and face-to-face $\pi-\pi$ interactions. The Cu^{II} atom, which lies at a center of inversion, has a distorted octahedral geometry, where the equatorial plane is composed of four N atoms belonging to two bidentate 4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole ligands, and the axial positions are occupied by two O atoms of two monodentate nitrate anions.

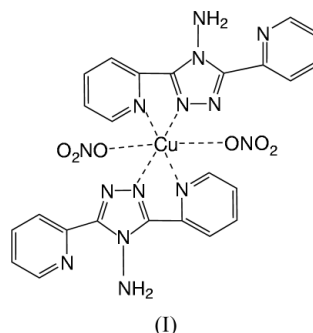
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Comment

The 1,2,4-triazole system is able to bridge paramagnetic metal centers, providing compounds with remarkable magnetic properties (Tang *et al.*, 2001). The presence of additional 2-pyridyl groups in 1,2,4-triazoles enhances the stability of the resulting complexes due to the chelate effect (Klinge & Brooker, 2003). Thus, 4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole (hereafter abbreviated to abpt) is able to act as a bis-bidentate bridging ligand between metal centers (van Koningsbruggen *et al.*, 1995), but it usually behaves as a bidentate ligand to give mononuclear complexes with interesting physical properties. For example, this ligand has recently been investigated for its capacity to give spin crossover iron(II) compounds (Moliner *et al.*, 1999; Moliner *et al.*, 2001; Gaspar *et al.*, 2003). In the framework of our current research on first-row transition metal complexes containing *N*-heterocyclic terminal ligands (Castillo *et al.*, 2001, 2003), we have obtained the title compound, (I).



As shown in Fig. 1, the Cu^{II} atom of (I) is located on an inversion center and is surrounded by two *N,N'*-bidentate abpt ligands and two weakly coordinated nitrate anions, which result in a tetragonally elongated CuN_4O_2 chromophore. The neutral abpt ligand coordinates to the metal center *via* atom N1 of the triazole moiety [$\text{Cu1}-\text{N1} = 1.899(3)\text{ \AA}$] and atom

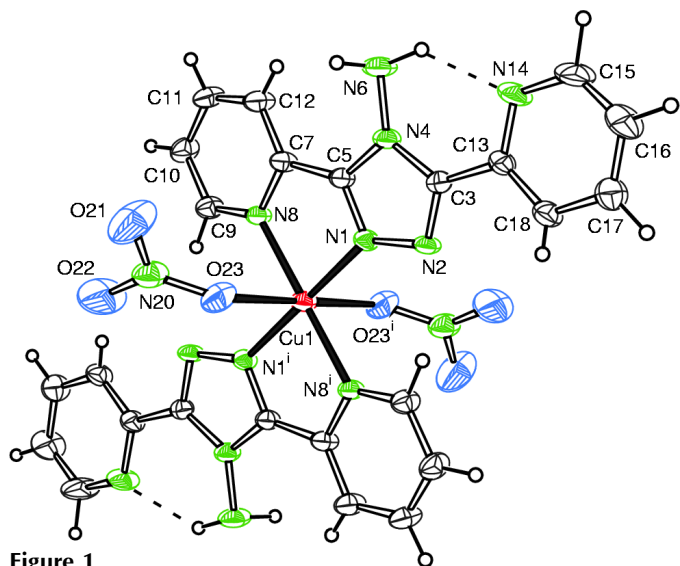


Figure 1
The structure of (I), with 30% probability displacement ellipsoids. Intramolecular N—H...O hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $-x, -y, -z$.]

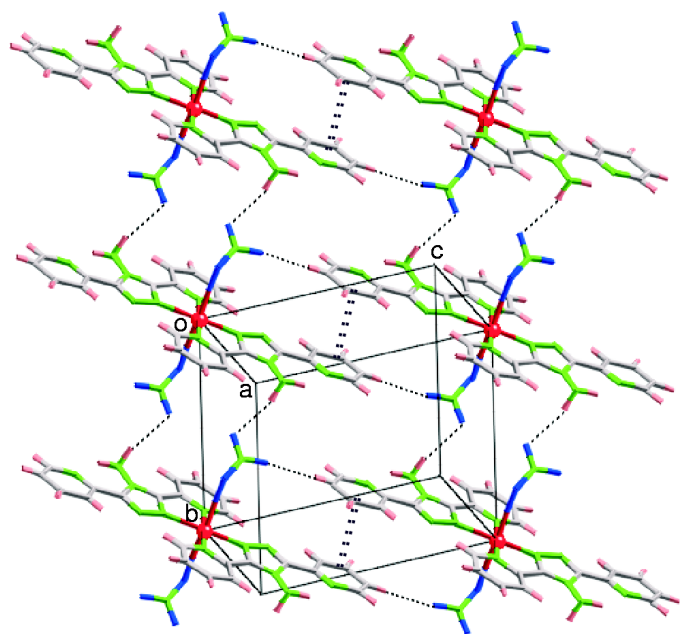


Figure 2
Packing diagram of (I), showing intermolecular hydrogen bonds (dashed lines) and face-to-face aromatic interactions (double dashed lines).

N8 from the adjacent pyridyl group [Cu1—N8 = 1.983 (3) Å], forming a five-membered chelate ring with an N1—Cu1—N8 bite angle of 86.1 (1)°. These four atoms form the equatorial plane and the remaining potential donor atoms (N2 and N14) of the abpt ligand are uncoordinated. The octahedral coordination of the metal is completed by atoms O23 and O23ⁱ of two *trans*-coordinated nitrate anions at a quite long bond distance of 2.541 (3) Å (symmetry code as in Table 1). The abpt ligand is essentially planar. The planes through the coordinated and non-coordinated pyridyl rings make dihedral angles of 6.5 (2) and 9.2 (2)°, respectively, with the triazole ring, while they are inclined at an angle of 4.8 (2)° with respect

to one another. These structural parameters are closed to those reported for analogous Cu^{II} complexes containing the bidentate abpt ligand (Cornelissen *et al.*, 1992; Jircitano *et al.*, 1997; van Koningsbruggen *et al.*, 1998). Both amine H atoms are hydrogen bonded; one binds intramolecularly to atom N14, which may contribute to the overall planarity of the abpt ligand, and it also appears to stabilize the non-coordinating pyridine ring in a *trans*-like conformation (Faulmann *et al.*, 1990; Cornelissen *et al.*, 1992; Kunkeler *et al.*, 1996). The second amino H atom is connected to a free atom O21 belonging to a nitrate anion of a neighboring monomer (Fig. 2), resulting in infinite hydrogen-bonded chains running along the *b* axis. These chains are crosslinked by means of weak intermolecular C—H...O interactions and offset face-to-face π – π stacking interactions between uncoordinated pyridine rings belonging to adjacent molecules, with a centroid–centroid distance of 3.84 (1) Å and a lateral displacement of 1.31 Å (Janiak, 2000).

Experimental

A methanol solution (35 ml) of Cu(NO₃)₂·3H₂O (0.048 g, 0.2 mmol) was added dropwise to a methanol solution (10 ml) of abpt (0.047 g, 0.2 mmol). Light-blue single crystals of (I) were grown by the slow evaporation of the mixture at room temperature (yield 20–30%, based on metal). Elemental analysis (%) found (C/H/N/Cu): 43.48, 3.07, 29.48, 9.54; calculated for C₂₄H₂₀CuN₁₄O₆: 43.41, 3.04, 29.53, 9.57.

Crystal data

[Cu(NO₃)₂(C₁₂H₁₀N₆)₂]
 M_r = 664.09
 Triclinic, $P\bar{1}$
 a = 6.940 (1) Å
 b = 9.319 (2) Å
 c = 10.765 (2) Å
 α = 99.36 (1)°
 β = 94.86 (2)°
 γ = 106.27 (2)°
 V = 653.2 (2) Å³
 Z = 1
 D_x = 1.688 Mg m⁻³

D_m = 1.69 (1) Mg m⁻³
 D_m measured by flotation in a mixture of carbon tetrachloride and bromoform
 Mo $K\alpha$ radiation
 Cell parameters from 6086 reflections
 θ = 3.3–30.0°
 μ = 0.91 mm⁻¹
 T = 293 (2) K
 Plate, light blue
 0.20 × 0.10 × 0.02 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
 ω scans
 Absorption correction: numerical (CrysAlis RED; Oxford Diffraction, 2003)
 T_{\min} = 0.884, T_{\max} = 0.973
 5600 measured reflections

3102 independent reflections
 1192 reflections with $I > 2\sigma(I)$
 R_{int} = 0.051
 θ_{max} = 28.0°
 h = $-8 \rightarrow 9$
 k = $-12 \rightarrow 11$
 l = $-11 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.046
 $wR(F^2)$ = 0.078
 S = 0.81
 3102 reflections
 205 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0159P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.34 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.32 \text{ e } \text{Å}^{-3}$

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.899 (3)	Cu1—O23	2.541 (3)
Cu1—N8	1.983 (3)		
N1—Cu1—N1 ⁱ	180	N8—Cu1—N8 ⁱ	180
N1—Cu1—N8	86.1 (1)	N8—Cu1—O23	87.4 (1)
N1—Cu1—N8 ⁱ	93.9 (1)	N8—Cu1—O23 ⁱ	92.6 (1)
N1—Cu1—O23	87.0 (1)	O23—Cu1—O23 ⁱ	180
N1—Cu1—O23 ⁱ	93.1 (1)		

Symmetry code: (i) $-x, -y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N6—H61 ⁱ ···N14	0.97	2.10	2.901 (4)	139
C9—H9 ⁱ ···N2 ⁱ	0.93	2.13	2.923 (4)	143
N6—H62 ⁱ ···O21 ⁱⁱ	0.96	2.26	3.186 (5)	161
C10—H10 ⁱ ···O21 ⁱⁱⁱ	0.93	2.57	3.454 (6)	160
C16—H16 ⁱ ···O22 ^{iv}	0.93	2.32	3.247 (5)	173
C18—H18 ⁱ ···O23 ^v	0.93	2.21	3.043 (4)	149
C11—H11 ⁱ ···O22 ^{vi}	0.93	2.52	3.447 (5)	172

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, 1-y, -z$; (iii) $1+x, y, z$; (iv) $x-1, y, 1+z$; (v) $-1-x, -y, -z$; (vi) $1-x, 1-y, -z$.

The amino H atoms were located in difference Fourier maps and refined as riding on their carrier N atoms, in their as-found positions, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. The C-bound H atoms were positioned geometrically, with $C-H = 0.93 \text{ \AA}$, and were included in the refinement in the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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